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Extended Summaries Pesticides in Food and Drink

The following are extended summaries based on papers presented at the 1st European Pesticide Residue Workshop, 'Pesticides in Food and Drink', held at Alkmaar, The Netherlands on 10–12 June, 1996. They are entirely the responsibility of the authors and do not necessarily reflect the views of the Editorial Board of Pesticide Science.

The Spanish Pesticide Residue Monitoring Programme: Design and Results

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Introduction

The surveillance of the presence of pesticide residues in foods, especially in vegetable products, is a growing preoccupation with Spanish producers, traders, and consumers, and it receives special attention, as part of the responsibilities of Crop Protection Services in the diverse Autonomous Communities.

However the actual regulation is contained in the Royal Decree 280/1994,[1] where the maximum residue levels (MRL) and their control in vegetable products are established; as well as fixing MRL for the 395 active ingredients registered for use in Spain, it incorporates the MRL accepted within the European Union. A surveillance system of the components and amounts of the pesticide residues in vegetable products is made through sample inspections, to avoid the distribution of products with pesticide residues that exceed the MRL. It has been completed with the inclusion of the Order of 27 February 1996 which contains revised MRLs for 42 active ingredients.[2]

The Autonomous Communities are in charge of establishing the continuing control of pesticide residues in the market. The surveillance of products imported from countries outside the EU is the responsibility of the Ministry of Agriculture, Fishing and Food in collaboration with the Ministry of Health and Consumption.

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Some Communities have set up their own regulations to develop these activities that are their responsibility. For example, in Valencia Community the Decree 134/1995 establishes the monitoring programme of pesticide residues in plant products, in which are included two subprogrammes, warehouse surveillance and market surveillance. Regional Commission Officials of Agriculture and Environment and of Health and Consumption have established the sampling and analytical methods, defined responsibilities and have power to impose strict sanctions.

In any case, whether based on their own regulations[3] or on Royal Decree 280/1994, since 1991 practically all Communities have developed monitoring programmes whose results are studied in the Spanish Working Group of Pesticide Residues. Their results are sent to Subdirection General of Plant Protection and form the basis of the annual report sent to the EU.

Sampling

Samples are taken during production, on collection from the producer, at delivery to the wholesale horticultural produce/fruit centres or warehouses or at the selling point, but always before the produce is offered for sale. Most are taken from warehouses.

The number of samples for each vegetable product is proportional to the production volume, also considering seasonal and geographical distribution, though the proportion can be different in each community.

Usually there are three levels of sampling: Informative, Confirmative and Regulatory. Informative samples are taken at random and represent the majority of the samples. When the MRLs in the Informative samples are exceeded, Confirmative samples are taken from several parts of the same batch of product in the same place. Regulatory sampling is an official sampling which occurs when the improper use of pesticides is confirmed and these imply the application of a sanction.

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Occasionally, direct movement from informative to Regulatory sampling occurs.

The samplings are carried out by the Official Services of the Autonomous Communities and the analyses are performed in Official Laboratories. The samples should satisfy all requirements with respect to representativeness, amount, storage, transport, etc., and a sample information sheet is enclosed.

Analytical methods

The 16 laboratories of the Autonomous Communities that carry out control of samples in their regional area are composed of the Working Group of Residues Laboratories from MAPA (Ministry of Agriculture, Fishing and Food). This commission develops, proposes and performs the analytical methods for pesticides, and these are used in every laboratory, as well as instrumentation suitable for analysis of the different groups of compounds. The methods described in the Surveillance Procedure Manual, are:

(a) A GC-multiresidue method, based on extraction with ethyl acetate followed by clean-up gel permeation chromotography (GPC).[4] This is used to analyse organophosphorus, organochlorine and nitrogen compounds and pyrethroids. The Luke method[5] is also included as an optional method and involves analysis by gas chromatography with electron capture (GC-ECD), flame photometric (GC-FPD), and thermionic-specific (GC-TSD) detection.

(b) Two methods for dithiocarbamates,[6,7] a headspace and a spectrophotometric method to determine the carbon disulfide liberated from the dithiocarbamate.

(c) An analytical method for benzimidazoles involving extraction with ethyl acetate, partition (acid/base) and determination by HPLC with UV diode-array detection.[8]

(d) A multiresidue method for *N*-methylcarbamates.[9,10] The sample is extracted with acetonitrile saturated with hexane, the extract sample is passed through an Extrelut 20 column and cleaned up further by SPE using an aminopropyl column. Determination is carried out by HPLC using post-column derivatization and fluorescence detection.

From the beginning of this year, in Valencia, the 'miniaturised' Luke method has been used. From a stock extract, aliquots are taken for analysis using various multiresidue detection systems. Some advantages of the 'mini-Luke' method are simplicity and reduction of analysis time and solvent volume, all of which reduce costs.

Sample extracts are analysed via GC-ECD, GC-NPD, and GC-FPD, and that allows analysis of about 120 pesticides. As a rule, when pesticides residues are above the tolerances, results are confirmed by GC-ITD(MS) using two different capillary columns and two different detectors.

From the stock extract, two HPLC methods are used routinely in this laboratory to analyse for *N*-methylcarbamates and benzimidazoles following clean-up via automated solid phase (SPE) 'on-line' facilities. Another sensitive method used for screening for benzimidazoles employs the ELISA technique[13] without problems with matrix effects and solvents. Samples giving positive results in the ELISA analysis are checked using HPLC.

Quality control

The multiresidue and specific analytical methods used have to be approved and developed by the Working Group of Laboratories. All standards and stock solutions are checked for purity, accuracy, storage, stability, etc., according to the rules established in the Quality Manual.

During routine GC analysis, an standard control is always included in the sample series. This is prepared freshly each day by adding the various standard mixtures according to a representative matrix type, in order to avoid matrix effects.

In general, when a pesticide residue exceeds an MRL, a repeat analysis is carried out and, at the same time, the results are checked by GC-MS. The laboratories have to participate in inter-laboratory checks each year.

Last year (1995) the process for accreditation of official laboratories by ENAC (National Spanish Accreditation Unit) was established.

Results and discussion

Data regarding total numbers of samples tested in Spain and the percentage with residues >MRL are in Table 1.

The percentages of violating samples are relatively low and are similar to those in other countries. Percentages of samples without detectable residues and of those with residues below the MRLs in the years 1993, 1994 and 1995 were 67.0, 61.8 and 61.4 and 30, 35 and 35, respectively.

However, the data have only limited value because some laboratories have trouble with investment for equipment and personnel to control their monitoring programme. Such laboratories can apply only the multi-

TABLE 1
Number of Samples Tested and Percentage of Violative Samples

Year	*Nº. samples*	Samples with >MRL (%)
1991	8082	5.65
1992	7180	5.41
1993	2988	3.01
1994	3234	3.18
1995	3051	3.57

residue GC method and with a limited number of pesticides and not the other three methods (Dithiocarbamates and HPLC methods). For that reason, the number of violating samples may be somewhat lower. Some laboratories are able to use the HPLC methods, in some cases.

Although the numbers of violating cases vary a lot according to crops, years and geographical areas the following occur most commonly (Figs. 1 and 2).

—Methamidophos content in various horticultural crops, including some where its use is not authorised (aubergines, courgettes, green beans, watermelon, melon, lettuce, chinese leaves), as well as the authorised use (peppers, tomatoes, melon), exceeds its MRL. In some cases it can appear as a metabolite from acephate.

—Violations provoked by acephate in various crops, in authorised use (tomatoes, green beans, cucumber) and in unauthorised use (watermelon, melon, and courgette).

—There have been repeated cases of exceeding the MRL of chlorpyrifos in some crops (oranges, bananas, cabbages, artichokes, carrots, stems) and in different areas.

—The fungicide chlorothalonil has been detected at >MRL in distinct areas, especially in lettuces, leaf crops and cabbages.

—Dithiocarbamates have caused problems in some vegetables (onions, tomatoes, cabbages), fruits (peaches, pears and grapes) and others (olives, sunflowers).

—MRLs for endosulfan have been exceeded in tomatoes, peppers, lettuces, cabbages and fruits (peaches and tangerines).

Other pesticides giving problems, but to a lesser degree, are: chlorfenvinphos, lindane, cypermethrin,

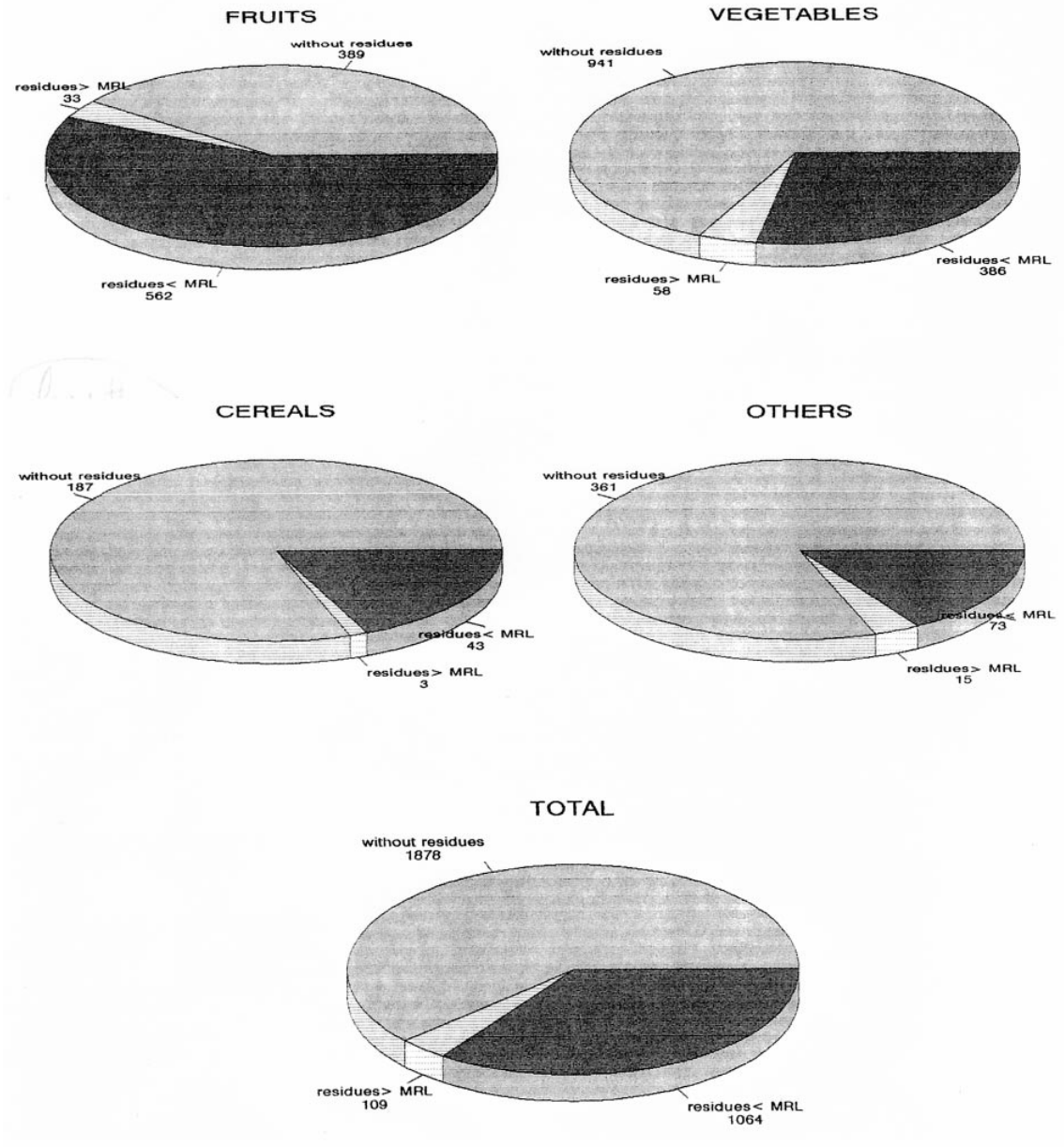

Fig. 1. Summary of results of the 1995 monitoring programme.

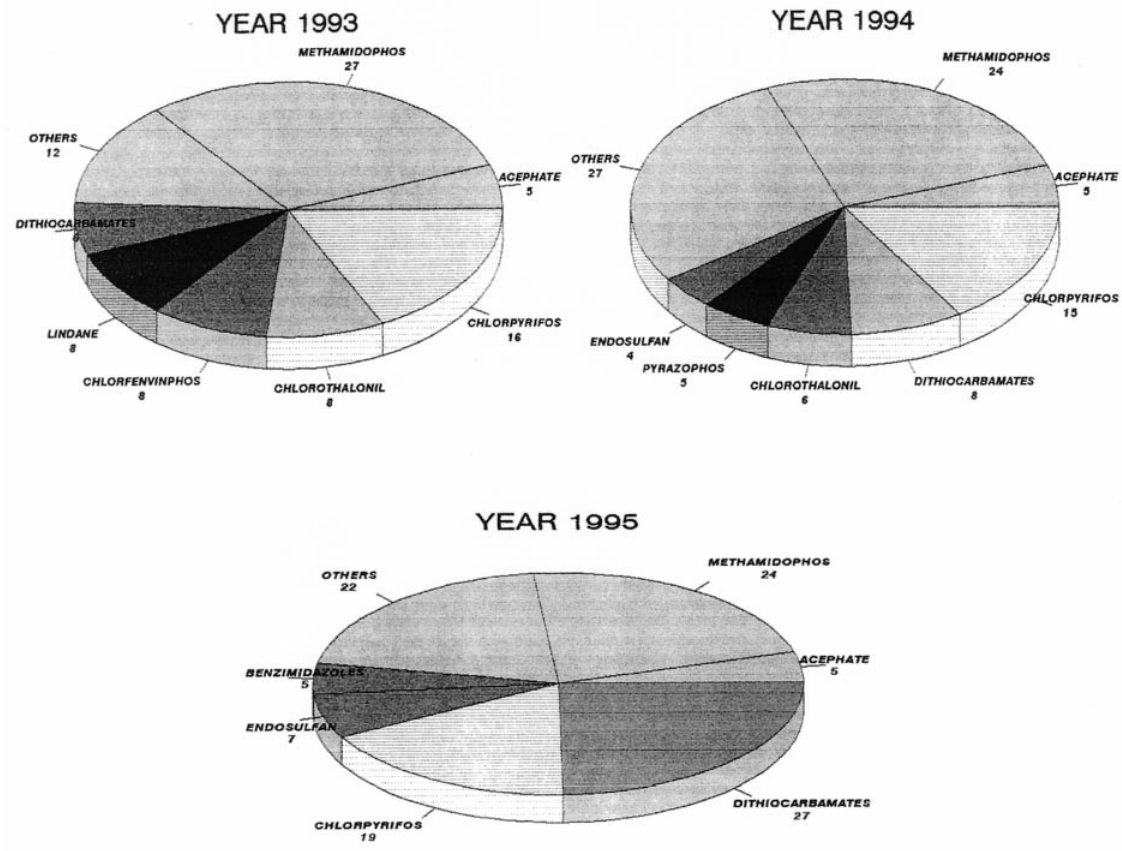

Fig. 2. Pesticides detected in violative samples.

procymidone, azinphos-methyl, bifenthrin, bromopropylate, dimethoate, parathion, methidathion, nuarimol, penconazole, oxadixyl, chorpyrifos-methyl, iprodione, deltamethrin, cyfluthrin, ethiofencarb, fenamiphos, fenarimol, methiocarb, pirimiphos-methyl, pyrazophos, tebuconazole, dicloran, dicofol, benzimidazoles, permethrin, parathion-methyl, diazinon, imazalil, thiabendazole and fenpropathrin.

An important proportion of the problems results from pesticide/vegetable combinations whose MRL is at the limit of detection of that pesticide. This problem can increase in the future if MRLs are not established in the EU directives for all possible pesticide/vegetable combinations, especially in minor crops.

Conclusions

The results of the Spanish pesticides residues monitoring programme, in terms of residue levels and numbers of samples containing residues at >MRL, varied greatly in the individual pesticides detected and in the number of violative cases, according to the year and the region from which the samples emanated. However, during the last years the proportion of violations has stabilised at between 3 and 5% of the samples analysed, and the proportion of samples with detectable residues was between 33 and 38.5%.

The pesticides that caused most violations were: methamidophos, acephate, chorpyriphos, dithiocarbamates, chlorothalonil, endosulfan, and benzimidazoles. In some crops, those violations were due to the use of unauthorised compounds, but in other cases they were due to improper use of pesticides (e.g. dosage exceeded or crops harvested earlier than the prescribed interval between treatment and harvest). There is an important proportion of violations, where the MRL is very close to the limit of detection of the compound.

The majority of violative cases were found in vegetables, followed by fruits, other crops representing a minor proportion.

In addition to the monitoring programme, other activities were carried out in order to reduce the content of pesticide residues in vegetable products. These activities consisted of: study of degradation curves of pesticides of great interest, design of special strategies of plant protection, and promotion of integrated pest control by farmer groups with technical support of Official Services and economic assistance from the Administration.

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